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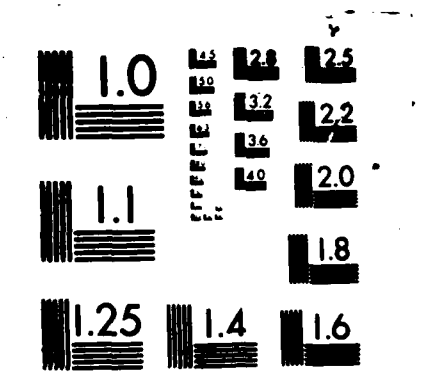

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R. Laine, Y. Blum, A. Chow, and K. Schwartz

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FINAL REPORT

For

Transition-Metal-Catalyzed Polymerization of Silazanes as a Route to the Preparation of Silicon-Carbide-Nitride Fibers. N00014-84-C-0392 (SRI Project No. 7605)

and

FINAL REPORT

For

Advanced Methods for the Preparation of Preceramic Polymers and Their Transformation into Silicon Nitride Fibers. N00014-85-C-0668 (SRI Project No. 8997)

Richard M. Laine, Yigal D. Blum, Andrea W. Chow and Kenneth B. Schwartz
SRI International, Menlo Park, CA 94025

SRI International®
333 Ravenswood Ave • Menlo Park, CA 94025
415 326-6200 • TWX 910-373-2046 • Telex 334-486

Summary of Research Objectives and Significant Results

The primary goal for both projects is to develop synthetic routes to tractable preceramic polysilazanes that can be spun into preceramic fibers and pyrolytically transformed into silicon nitride or silicon carbide-nitride fibers based on novel catalytic processes discovered at SRI. The research program is divided into three separate Tasks. Our efforts, in the first task, are directed towards optimizing the polymer synthesis process(es) through detailed studies of the kinetics and mechanisms of the catalytic reaction(s) that promote polymer formation. Research in the second task focusses on rheological characterization of polymers produced in the first task and development and refinement of polymer spinning procedures. The third task efforts are concerned with optimizing the process whereby the polysilazanes produced in Task 1 and shaped in Task 2 are pyrolytically transformed into ceramic materials and the characterization of the ceramic products.

In the course of our studies, we have detailed the kinetics and mechanisms of the transition metal catalyzed cleavage of Si-N bonds and the dehydrocoupling process whereby Si-N bonds are formed from Si-H and N-H bonds using simple model systems (Technical reports 1, 2, 4-6, 9). We have identified ruthenium as the best catalyst for dehydrocoupling following a survey of potential transition metal catalysts. To date, we find that the best catalyst for this process is the species $(Et_3Si)_2Ru_2(CO)_8$. We have also studied on the kinetics of the dehydrocoupling polymerization reaction (Technical report 7) as a prelude to fiber spinning efforts. We have learned to control the viscoelastic properties of the polymer through control of the polymerization reaction conditions. As a result of these studies, we have learned how to continuously extrude thick (100-300μm) fibers of the precursor and hand draw fibers as thin as 10 μm (Technical report 8).

Studies of the effects of reaction conditions and the pyrolysis reaction chemistry of a series of related polysilazane polymers have provided us with an understanding of how to optimize the ceramic yields and control the selectivity to ceramic products (Technical report 3). We have also established some understanding of the kinetics of the process(es) that occur during the transformation of the preceramic into a ceramic product. We find that the macromolecular properties control the ceramic yield whereas the molecular properties control selectivity to ceramic product. We conclude that molecular design can be used to control selectivity to ceramic product.

We have learned to use the preceramic polymers to form uniform, corrosion resistant coatings of silicon nitride on steel, aluminum and magnesium. We have also learned to coat glass and graphite with silicon nitride. The process we have developed is a simple dipcoat process which should also be useful in a spin coating process.

The same polysilazane precursors have been found to be extremely useful as binders for silicon nitride powders. Unlike common organic binders, the precursors actually cause densification of powder to occur upon pyrolysis to 800°C. This could eventually permit processin of silicon nitride powders at much lower temperatures than are currently required.

LIST OF PUBLICATIONS AND SUBMITTED MANUSCRIPTS

Papers Published in Refereed Journals

1. Catalytic Methods for the Synthesis of Oligosilazanes., Y. D. Blum and R. M. Laine, Organomet. (1986) 5, 2801-2086.

Papers Submitted to Refereed Journals

1. Catalytic Synthesis of Oligosilazanes. 2., C. Biran, Y. D. Blum, R. M. Laine, R. Glaser, and D. S. Tse; J. Molec. Cat., submitted July, 1987

2. Polymerization Kinetics of Polysilazanes by Transition Metal Catalyzed Dehydrocoupling Reaction. A. W. Chow, R. D. Hamlin, Y. Blum and R. M. Laine, J. Polymer Sci., submitted July, 1987.

3. Does Molecular Design Play a Role in the Conversion of Preceramic Polymers into Ceramic Materials?, R. M. Laine and Y. D. Blum, Science; submitted July, 1987.

Book Chapters Published

1. "A New Catalytic Method for Producing Preceramic Polysilazanes." Y. D. Blum, R. M. Laine, K. B. Schwartz, D. J. Rowcliffe, R. C. Bening and D. B. Cotts, Better Ceramics Through Chemistry II, Mat. Res. Symp. Proc. Vol. 73, C. J. Brinker, D. E. Clark, and D. R. Ulrich, Eds. (1986) pp 389-394.

2. "Thermal Conversion of Preceramic Polysilazanes to Si_3N_4: Characterization of Pyrolysis Products." K. B. Schwartz, D. J. Rowecliffe, Y. D. Blum, and R. M. Laine, Better Ceramics Through Chemistry II, Mat. Res. Symp. Proc. Vol. 73, C. J. Brinker, D. E. Clark, and D. R. Ulrich Eds. (1986) pp 407-412.

Book Chapters Submitted for Publication

1. Organometallic Polymers as Precursors to Ceramic Materials: Silicon Nitride and Silicon Oxynitride, R. M. Laine, Y. D. Blum, R. D. Hamlin and A. Chow, in "Ultrastructure Processing of Ceramics, Glasses and Composites II" D. J. Mackenzie and D. R. Ulrich Eds.: John Wiley and Sons. Inc. in press.

2. Synthetic Routes to Oligo- and Polysilazanes. Polysilazane Precursors to Silicon Nitride. R. M. Laine, Y. D. Blum, D. S. Tse, and R. Glaser, in "Inorganic and Organometallic Polymers" American Chemical Society Symposium Series, K. Wynne and M. Zeldin Eds., in press.

Patents

1. "Method of Producing Polysilazanes" R. M. Laine and Y. Blum, U. S. Patent No. 4, 612, 383 (1986).

Participating Personnel

Mr. Robert C. Bening
Dr. Claude Biran
Dr. Yigal D. Blum
Dr. David B. Cotts
Dr. Andrea W. Chow
Mr. Alan Dodge
Dr. Robert Glaser
Mr. Richard D. Hamlin
Dr. Richard M. Laine
Ms. Penni Lundquist
Dr. David J. Rowcliffe
Dr. Kenneth B. Schwartz
Ms. Doris S. Tse

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